(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 709 345 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
01.05.1996 Bulletin 1996/18

(51) Int Cl.6: C03C 3/247, C03C 4/12

(21) Application number: 95307573.6

(22) Date of filing: 24.10.1995

(84) Designated Contracting States:
DE FR GB

(30) Priority: 31.10.1994 JP 266759/94

(71) Applicant: SUMITA OPTICAL GLASS, INC.
Urawa-shi, Saitama-ken (JP)

(72) Inventor: Otsuka, Masaaki,
c/o Sumita Optical Glass Inc.
Urawa-shi, Saitama-ken (JP)

(74) Representative:
Baverstock, Michael George Douglas et al
BOULT, WADE & TENNANT
27 Furnival Street
London, EC4A 1PQ (GB)

(54) Tb- or Eu-containing fluorophosphate fluorescent glass

(57) A fluorescent glass capable of converting invisible ultraviolet rays into visible rays with high efficiency and available, for example, for controlling the optical axis of a laser beam such as an excimer laser has a chemical composition comprising, at least, phosphorus (P), oxygen (O) and fluorine (F), and further containing Tb or Eu as a fluorescent agent, and may specifically comprise in terms of atoms for making up the glass (mol %) :

P	1 ~ 15
Al	1 ~ 18
Mg	0 ~ 12
Ca	0 ~ 18
Sr	0.5 ~ 21
Ba	0.5 ~ 28
Zn	0 ~ 3.5
R	0 ~ 10
Ln	0.8 ~ 8
Ln'	0 ~ 6.5
Ce	0 ~ 0.2
O	4 ~ 55
F	15 ~ 70

wherein Ln is Tb or Eu, and Ln' is at least one atom selected from the group consisting of Y, La, Gd and Yb and R is at least one atom selected from the group consisting of Li, Na and K.

EP 0 709 345 A1

Description

This invention relates to a Tb- or Eu-containing fluorophosphate fluorescent glass capable of converting invisible ultraviolet rays into visible rays with high efficiency and available for controlling the optical axis of a laser beam such as excimer laser.

Phosphors using rare earth elements have been used widely up to the present time, mainly as phosphors for, for example, lamps and color picture. of late, materials for the anti-Stokes-wise wavelength conversion of infrared light into visible light have been studied extensively, for example, with a view to application to laser materials.

Tb ion, which shows the strongest fluorescence (green) in the visible region, among the rare earth element ions, has been put to practical use as intensifying screens, projection cathode-ray tubes, high color rendering fluorescent lamps, etc. Eu ion showing a fluorescence with a narrow spectrum width in the red region has been put into practice as color picture tubes, high color rendering fluorescent lamps, etc. As described above, a phosphor using Tb or Eu has already been put to practical use, but such a phosphor is an opaque material which is obtained by coating a suitable carrier with a powdered phosphor to thus give only a superficial emission.

As such a glass utilizing the fluorescence of Tb or Eu, there are used those described in Japanese Patent Publications Nos. 27047/1982 and 27048/1982.

However, the glasses described in these publications, for example, in Japanese Patent Publication No. 27047/1982 contain only at most 1.5 mol % of Eu_2O_3 as a fluorescent agent. In the case of Japanese Patent Publication No. 27048/1982, only at most 1.5 mol % of Tb_2O_3 is included as a fluorescent agent and other rare earth elements such as Eu_2O_3, Dy_2O_3, Sm_2O_3 and Tm_2O_3, are simultaneously added for imparting a multi-coloring property.

When varieties of fluorescent agents are present in admixture, in general the fluorescent intensity is decreased by their interaction and a high efficiency emission cannot be obtained.

It is an object of the present invention to provide a Tb- or Eu-containing fluorophosphate fluorescent glass whereby the above described problems of the prior art can be overcome.

It is another object of the present invention to provide a Tb- or Eu-containing fluorophosphate fluorescent glass in which a large quantity of Tb or Eu can be incorporated, concentration quenching scarcely occurs and a strong fluorescence is exhibited in the visible region by irradiation of ultraviolet rays such as in an excimer laser.

These objects can be attained by a Tb- or Eu-containing fluorophosphate fluorescent glass capable of exhibiting fluorescence in the visible region, having a chemical composition comprising, at least, phosphorus (P), oxygen (0) and fluorine (F), and further containing Tb or Eu as a fluorescent agent.

The accompanying drawings illustrate the principle and merits of the present invention.

Fig. 1 is a graph showing a fluorescent spectrum of Tb ion when the glass prepared in Example 1 is excited by an ultraviolet ray of 250 nm.

Fig. 2 is a graph showing a fluorescent spectrum of Eu ion when the glass prepared in Example 20 is excited by an ultraviolet ray of 250 nm.

Generally, the fluorescence of rare earth ions tends to be subject to concentration quenching and the basic absorption of a glass matrix at the short wavelength side is shifted to the long wavelength side with the increase of amounts of rare earth elements. Accordingly, capture of excited energy takes place by the non-luminescence center, so that a phosphor material presenting a strong fluorescence cannot be obtained. This problem can be solved by the present invention.

Specifically, according to the present invention, there is provided a Tb- or Eu-containing fluorophosphate fluorescent glass capable of presenting fluorescence in the visible region, having a chemical composition comprising,at least, phosphorus (P), oxygen (0) and fluorine (F), and further containing Tb or Eu as a fluorescent agent. Specifically, the Tb- or Eu-containing fluorophosphate fluorescent glass is represented, in term of atoms for making up the glass, by the following chemical composition (mol %):

P	1 to 15 %,
Al	1 to 18 %
Mg	0 to 12 %,
Ca	0 to 18 %
Sr	0.5 to 21 %,
Ba	0.5 to 28 %
Zn	0 to 3.5 %,
Ln	0.8 to 8 % (Ln: Tb or Eu),
Ln'	0 to 6.5 % (Ln': at least one atom selected from Y, La, Gd and Yb)
Ce	0 to 0.2 %
R	0 to 10 % (R: at least one atom selected from Li, Na and K),
0	4 to 55 % and

F 15 to 70 %

The reasons for limiting the composition range of each component of this fluorophosphate fluorescent glass to that described above are as follows:

P is a glass-forming component, which is present in a proportion of 1 to 15 %, since if less than the lower limit, glass formation is difficult, while if more than the upper limit, durability deteriorates. The preferred range is 2 to 13 %.

Al is a component for increasing the viscosity of the glass and suppressing crystallization, which is present in a proportion of 1 to 18 %, since if more than the upper limit, the melting property is reduced and the glass is unstable. The preferred range is 2 to 12 %.

Mg, Ca, Sr, Ba and Zn are components for improving the melting property of the glass. If more than the above described ranges, the glass is unstable and tends to crystallize. The preferred ranges are respectively 0 to 6 % of Mg, 0 to 9 % of Ca, 1.5 to 12 % of Sr, 1.5 to 17 % of Ba and 0 to 2 % of Zn.

R (at least one atom selected from Li, Na and K) acts to lower the melting temperature of a glass melt, which is present in a proportion of 0 to 10 %, since if exceeding the above described range, the water resisting property is reduced and the devitrification tendency is increased, thus rendering the glass unstable. The preferred range is 0 to 3 %.

Ln (Tb or Eu) is an important component capable of presenting fluorescence in the visible region by ultraviolet excitation. This component should be present in the above described proportion, since if less than the lower limit, sufficient fluorescence cannot be obtained, while if more than the upper limit, not only is the effect of concentration quenching increased, but also the solubilizing property worsens resulting in a tendency to retain melting residue. The preferred range is 0.8 to 5 %.

Ln' (at least one atom selected from Y, La, Gd and Yb) is a component for increasing the viscosity of the glass and suppressing crystallization. If more than the above described range, the melting property deteriorates, thus tending to form a melting residue. The preferred range is 0 to 4 %.

Ce is a component acting as a sensitizer of the fluorescent agent, but if exceeding the above described upper limit, this effect is decreased.

Production of the Tb- or Eu-containing fluorophosphate fluorescent glass according to the present invention is carried out by mixing the corresponding raw material compounds in a proportion of the desired composition, for example, aluminum phosphate, strontium fluoride, barium fluoride and terbium oxide, melting the resulting mixture in the air at a temperature of 900 to 1300 °C for 2 to 3 hours and allowing the mixture to flow out into a metallic mold, followed by shaping.

The features and preferred embodiments of the present invention are described below:

(1) A Tb- or Eu-containing fluorophosphate fluorescent glass capable of presenting fluorescence in the visible region, having a chemical composition comprising, at least, phosphorus (P), oxygen (0) and fluorine (F), and further containing Tb or Eu as a fluorescent agent.

(2) The Tb- or Eu-containing fluorophosphate fluorescent glass, as described above in item (1), having the following chemical composition shown in Table 1 and represented in terms of atoms for making up the glass (mol %):

Table 1

P	2 ~ 13
Al	2 ~ 12
Mg	0 ~ 6
Ca	0 ~ 9
Sr	1.5 ~ 12
Ba	1.5 ~ 17
Zn	0 ~ 2
R	0 ~ 3
Ln	0.8 ~ 5
Ln'	0 ~ 4
Ce	0 ~ 0.2
O	4 ~ 55
F	15 ~ 70

wherein R is at least one atom selected from the group consisting of Li, Na and K; Ln is Tb or Eu; and Ln' is at least one atom selected from the group consisting of Y, La, Gd and Yb.

(3) The Tb- or Eu-containing fluorophosphate fluorescent glass, as described above in item (1), having the following chemical composition shown in Table 2 and represented in terms of atoms for making up the glass (mol %):

Table 2

P	5.8 ~ 14.5
Al	1.3 ~ 8.3
Mg	0 ~ 9.9
Ca	0 ~ 11
Sr	0.9 ~ 16.3
Ba	2.5 ~ 20.9
Y	0 ~ 4.4①
La	0 ~ 2.2①
Gd	0 ~ 5①
Yb	0 ~ 2.6①
Tb	0.8 ~ 8①
Ce	0 ~ 0.2
O	19.2 ~ 50.2
F	16.4 ~ 49.4

wherein the sum of elements①= 0.8 - 8 %.

(4) The Tb- or Eu-containing fluorophosphate fluorescent glass, as described above in item (1), having the following chemical composition show in Table 3 and represented in terms of atoms for making up the glass (mol %):

Table 3

P	9 ~ 13
Al	3 ~ 4.5
Mg	0 ~ 7.5
Ca	0 ~ 9
Sr	1.5 ~ 12
Ba	5 ~ 17
Y	0 ~ 3.3 ②
La	0 ~ 1.2 ②
Gd	0 ~ 2.2 ②
Yb	0 ~ 2 ②
Tb	1.5 ~ 5 ②
Ce	0 ~ 0.1
O	30 ~ 45
F	24 ~ 36

wherein the sum of elements②= 1.5 ~ 5 %.

Examples

The present invention will now be illustrated in greater detail by the following examples, but the present invention

and the merits thereof are not intended to be limited by the materials, compositions and production procedures described in these examples.

(Example 1)

Using the compounds shown in Table 4 as raw materials, the raw materials were mixed in a proportion by weight as in Sample No. 1, melted at 900 to 1300 °C, allowed to flow into a metallic mold and shaped to obtain a glass in stable manner.

The thus prepared glass was excited by an ultraviolet ray of 250 nm to obtain a fluorescent spectrum as shown in Fig. 1. The emissions at 489 nm, 543 nm, 583 nm and 620 nm correspond to the emissions of $^5D_4 \rightarrow {}^7F_6$, $^5D_4 \rightarrow {}^7F_5$, $^5D_4 \rightarrow {}^7F_4$ and $^5D_4 \rightarrow {}^7F_3$ of the Tb ion, which was observed as green with the naked eye.

(Examples 2 to 19)

Glasses were obtained stably by preparing raw materials in the proportions by weight shown in Tables 4 to 6, Samples 2 to 19 and melting the mixture in a similar manner to Example 1.

When the glasses obtained in Examples 2 to 19 were also excited by an ultraviolet ray of 250 nm, there were obtained spectra similar to Example 1, presenting green fluorescence.

(Examples 20 to 21)

Glasses were obtained stably by preparing raw materials in the proportions by weight shown in Table 6, Samples Nos. 20 and 21 and melting the mixture in a similar manner to Example 1.

When the glass prepared in Example 20 was excited by an ultraviolet ray of 250 nm, there was obtained a fluorescent spectrum as shown in Fig. 2.

The emissions at 591 nm and 614 nm in Fig. 2 correspond to the emissions of $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ of the Eu ion, which was observed as red with the naked eye.

In Tables 7 to 9 are shown the compositions (atom %) of the glasses prepared in Examples 1 to 21.

Table 4

(g)							
Raw Material	Sample No.						
	1	2	3	4	5	6	7
$Al(PO_3)_3$	19.5		30	3.1	18.1	17.1	24.9
$Mg(PO_3)_2$					9.9		
$Ca(PO_3)_2$							
$Sr(PO_3)_2$							
$Ba(PO_3)_2$		4.4		4.7		10	
$Zn(PO_3)_2$							
$LiPO_3$							
$NaPO_3$		4.4					
KPO_3							
AlF_3		32.2		34.5			
MgF_2		5.4		7.3	7.8	8	
CaF_2		15		13.7	14.7	15	
SrF_2	19.9	20.5	5	22.6	12.7	13	20
BaF_2	39.1	10	54.9	7	21.6	22	34.8
Tb_2O_3	21.5	7.8	4.9	6	9	9.8	6.2
Eu_2O_3							
Y_2O_3							
La_2O_3			2			5.1	
Gd_2O_3			3.2				14.2

Continuation of the Table on the next page

Table 4 (continued)

(g)							
Raw Material	Sample No.						
	1	2	3	4	5	6	7
Yb_2O_3					6.2		
CeO_2			0.05				
LiF							
NaF		0.3		1.1			
KF							

Table 5

(g)							
Raw Material	Sample No.						
	8	9	10	11	12	13	14
$Al(PO_3)_3$	19.2	25.5	18.7	20.2	17.1	19.7	19.7
$Mg(PO_3)_2$							
$Ca(PO_3)_2$			8				
$Sr(PO_3)_2$					8.1		
$Ba(PO_3)_2$						5.6	
$Zn(PO_3)_2$				9.9			
$LiPO_3$							
$NaPO_3$							
KPO_3	6.5						
AlF_3	15.3	16.3				12.9	
MgF_2	11.4	6	6.4		6.4	4.4	
CaF_2	8.8	26.4	12		12	18.2	
SrF_2	16.4	8.5	14.5	20	14.3	19.7	5
BaF_2	14.2	10.2	25.7	39.9	25.5	9.4	68.1
Tb_2O_3	8.3	7.1	13.5	9.8	16.6	7.4	4.4
Eu_2O_3							
Y_2O_3			0.9				
La_2O_3							
Gd_2O_3							2.8
Yb_2O_3							
CeO_2			0.3	0.2			
LiF						1.8	
NaF							
KF						1	

Table 6

(g)							
Raw Material	Sample No.						
	15	16	17	18	19	20	21
$Al(PO_3)_3$		25	14.9	25	30.3	25.8	18.7
$Mg(PO_3)_2$							
$Ca(PO_3)_2$	1.4						

Continuation of the Table on the next page

Table 6 (continued)

(g)							
Raw Material	Sample No.						
	15	16	17	18	19	20	21
$Sr(PO_3)_2$							
$Ba(PO_3)_2$	4.6						
$Zn(PO_3)_2$							
$LiPO_3$			3.8				
$NaPO_3$			6.2				
KPO_3	3.5						
AlF_3	34.7		14.5				22.4
MgF_2	3.3		2.7				5.5
CaF_2	11.9		6.8				9.7
SrF_2	21.5	27.1	26.7	40	12.9	15.3	15.6
BaF_2	11	32.9	18.3	25	39.8	43.9	21.8
Tb_2O_3	6.6	5	6.2	10	14.8		
Eu_2O_3						15	6.2
Y_2O_3		10					
La_2O_3							
Gd_2O_3					2.2		
Yb_2O_3							
CeO_2							
LiF							
NaF	1.3						
KF							

Table 7

(mol%)							
Glass Composition (atom)	Sample No.						
	1	2	3	4	5	6	7
P	9.2	2.1	12.7	1.9	9.8	8.7	11
Al	3.1	11	4.2	11.7	2.2	2.2	3.6
Mg		2.5		3.2	5.6	4.3	
Ca		5.5		4.9	5.9	6.4	
Sr	6.6	4.7	1.5	5	3.2	3.4	6.2
Ba	9.3	2.1	11.7	1.5	3.9	5.3	7.7
Zn							
Li							
Na		1.4		0.7			
K							
Y							
La			0.5			1.1	
Gd			0.7				3
Yb					1		
Tb	4.9	1.2	1	0.9	1.5	1.8	1.3
Eu							
Ce			0.01				
O	35	8.1	41.4	7.1	33.3	30.3	39.4
F	31.8	61.5	26.4	63.1	33.7	36.6	27.7

Table 8

(mol%)							
Glass Composition (atom)	Sample No.						
	8	9	10	11	12	13	14
P	7.6	7.6	9.6	11.8	8.9	7.3	9.5
Al	7.1	7.6	2.3	2.8	2.2	6.4	3.2
Mg	5.1	2.5	3.4		3.5	2	
Ca	3.1	8.9	6.4		5.3	6.5	
Sr	3.6	1.8	3.8	5.9	5	4.4	1.7
Ba	2.3	1.5	4.8	8.5	5	2	16.5
Zn				1.7			
Li						1.9	
Na							
K	1.5					0.5	
Y			0.3				
La							
Gd							0.7
Yb							
Tb	1.3	1	2.4	2	3.1	1.1	1
Eu							
Ce			0.05	0.05			
O	24.8	24.4	33	38.5	31.5	23.7	31.3
F	43.5	44.7	34	28.8	35.4	44.1	36.3

Table 9

(mol%)							
Glass Composition (atom)	Sample No.						
	15	16	17	18	19	20	21
P	2.4	10.4	8.1	10.3	12.9	11.3	6.2
Al	10.7	3.5	6.8	3.4	4.2	3.8	9.7
Mg	1.7		1.3				2.6
Ca	5		2.6				3.6
Sr	5.4	7.9	6.3	11.6	3.8	4.7	3.6
Ba	2.4	6.9	3.1	5.2	8.4	9.6	3.6
Zn							
Li			1.3				
Na	1		1.8				
K	1						
Y		3.2					
La							
Gd					0.4		
Yb							
Tb	1.1	1	1	2	3		
Eu						3.3	1
Ce							
O	8.9	37.6	25.9	34	42.9	38.7	20
F	60.5	29.5	41.9	33.5	24.4	28.6	49.7

Comparative Example 1

Raw materials were mixed in a proportion by weight, calculated from a glass composition of the prior art, i.e. 75 % of B_2O_3, 17 % of Na_2O, 2 % of Al_2O_3. 3.45 % of CaO, 1 % of La_2O_3, 0.05 % of Eu_2O_3 and 1.5 % of Tb_2O_3 (mol %) (32.9 % of B, 7.5 % of Na, 0.9 % of Al, 0.8 % of Ca, 0.4 % of La, 0.01 % of Eu, 0.7 % of Tb and 56.9 % of O by mol % representation of atoms making up the glass), melted at 1000 to 1200 °C, allowed to flow out into a metallic mold and shaped.

When the thus prepared glass was excited by an ultraviolet ray of 250 nm, there was obtained a spectrum similar to Example 1, presenting green fluorescence. However, the emission intensity was only 1/4 times as large as that of Example 1 even taking the highest peak at 543 nm.

Advantages of the Invention

The fluorescent glass of the present invention is capable of converting invisible ultraviolet rays into visually observable visible rays with high efficiency and is available for controlling the optical axis of a laser beam such as an excimer laser.

Claims

1. A Tb- or Eu-containing fluorophosphate fluorescent glass capable of exhibiting fluorescence in the visible region, having a chemical composition comprising, at least, phosphorus (P), oxygen (0) and fluorine (F), and further containing Tb or Eu as a fluorescent agent.

2. A Tb- or Eu-containing fluorophosphate fluorescent glass as claimed in Claim 1, wherein the glass has the following chemical composition (mol %):

P	1 to 15 %,
Al	1 to 18 %,
Mg	0 to 12 %,
Ca	0 to 18 %,
Sr	0.5 to 21 %,
Ba	0.5 to 28 %,
Zn	0 to 3.5 %,
Ln	0.8 to 8 %,
Ln'	0 to 6.5 %,
Ce	0 to 0.2 %,
R	0 to 10 %,
O	1 to 15 % and
F	15 to 70 %,

and Ln is Tb or Eu, Ln' is at least one atom selected from the group consisting of Y, La, Gd and Yb and R is at least one atom selected from the group consisting of Li, Na and K.

3. A Tb- or Eu-containing fluorophosphate fluorescent glass as claimed in Claim 1 or Claim 2, wherein the glass has the following chemical composition (mol %):

P	2 to 13 %,
Al	2 to 12 %,
Mg	0 to 6 %,
Ca	0 to 9 %,

Sr	1.5 to 12	%,
Ba	1.5 to 17	%,
Zn	0 to 2	%,
Ln	0.8 to 5	%,
Ln'	0 to 4	%,
R	0 to 3	%,
Ce	0 to 0.2	%,
O	4 to 55	% and
F	15 to 70	%.

and Ln is Tb or Eu, Ln' is at least one atom selected from the group consisting of Y, La, Gd and Yb and R is at least one atom selected from the group consisting of Li, Na and K.

4. The Tb- or Eu-containing fluorophosphate fluorescent glass as claimed in any one of Claims 1 to 3, wherein the glass has the following chemical composition (mol %):

P	5.8 to 14.5 %,
Al	1.3 to 8.3 %,
Mg	0 to 9.9 %,
Ca	0 to 11 %,
Sr	0.9 to 16.3 %,
Ba	2.5 to 20.9 %,
Y	0 to 4.4 %①
La	0 to 2.2 %①
Gd	0 to 5 %①
Yb	0 to 2.6 %①
Tb	0.8 to 8 %①
Ce	0 to 0.2 %,
O	19.2 to 50.2 % and
F	16.4 to 49.4 %,

the sum of the elements① being 0.8 to 8 %.

5. The Tb- or Eu-containing fluorophosphate fluorescent glass as claimed in any one of Claims 1 to 4, wherein the glass has the following chemical composition (mol %):

P	9 to 13 %,
Al	3 to 4.5 %,
Mg	0 to 7.5 %,
Ca	0 to 9 %,
Sr	1.5 to 12 %,
Ba	5 to 17 %,
Y	0 to 3.3 %②
La	0 to 1.2 %②
Gd	0 to 2.2 %②

Continuation of the Table on the next page

(continued)

Yb	0 to 2 %②
Tb	1.5 to 5 %②
Ce	0 to 0.1 %,
O	30 to 45 % and
F	24 to 36 %,

the sum of the elements ② being 1.5 to 5 %.

6. Use of a Tb- or Eu- containing fluorophosphate fluorescent glass as claimed in any one of claims 1 to 5 for controlling the optical axis of a laser beam.

7. Apparatus for producing a laser beam whenever comprising a Tb- or Eu- containing fluorophosphate fluorescent glass as claimed in any one of claims 1 to 5.

FIG. 1

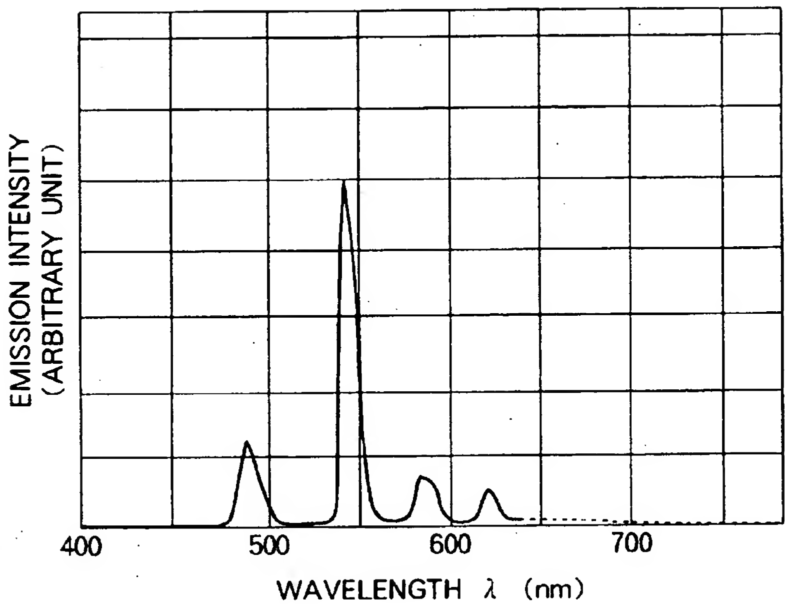
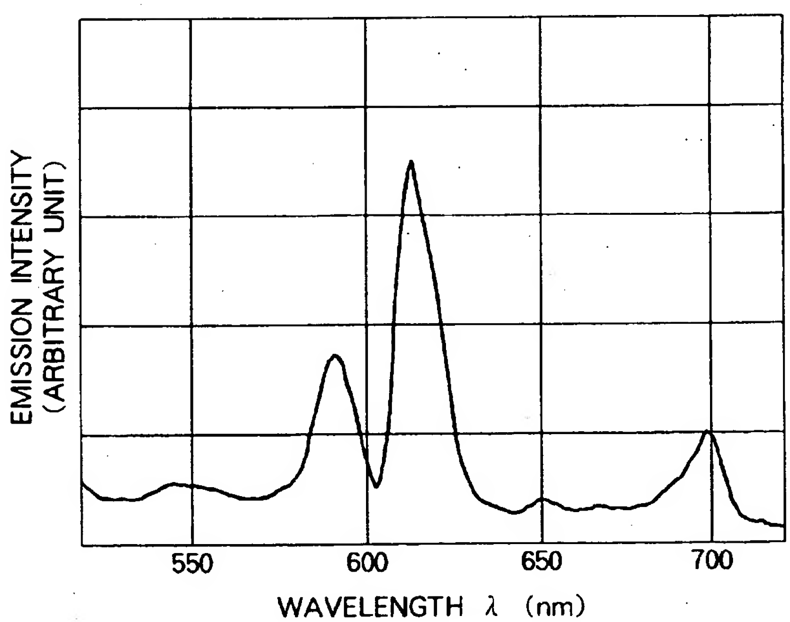

EMISSION INTENSITY
(ARBITRARY UNIT)
400
500
600
700
WAVELENGTH λ (nm)

FIG. 2


EMISSION INTENSITY
(ARBITRARY UNIT)
550
600
650
700
WAVELENGTH λ (nm)

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 95 30 7573

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	DATABASE INSPEC INSTITUTE OF ELECTRICAL ENGINEERS, STEVENAGE, GB Inspec No. 3536356, QI CHANGHONG ET AL 'Spectroscopic properties of Tb/sup 3+/ ions in fluorophosphate glass and possibility of obtaining visible laser light at room temperature' * abstract * & CHINESE JOURNAL OF LASERS, 20 APRIL 1989, CHINA, vol. 16, no. 4, ISSN 0258-7025, pages 227-232, ---	1-7	C03C3/247 C03C4/12
X	FR-A-2 381 724 (HOYA CORPORATION) 22 September 1978 * page 2, line 15 - page 3, line 37 * ---	1-3,6,7	
X	SOVIET JOURNAL OF GLASS PHYSICS AND CHEMISTRY, vol. 11, no. 6, December 1985 NEW YORK US, pages 409-415, T. V. BOCHAROVA ET AL. 'Correlation between the optical and ESR spectra of gamma-irradiated phosphate glasses ' * page 409; table 1 * ---	1,6,7	TECHNICAL FIELDS SEARCHED (Int.Cl.6) C03C
X	JOURNAL OF NON-CRYSTALLINE SOLIDS, vol. 142, no. 1-2, 1992 AMSTERDAM NL, pages 148-154, S. TANABE ET AL. 'Local structure of rare-earth ions in fluorophosphate glasses by phonon sideband and Mössbauer spectroscopy' * page 148 - page 149, left column * --- -/--	1,6,7	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	25 January 1996	Van Bommel, L

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 95 30 7573

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	SOVIET JOURNAL OF GLASS PHYSICS AND CHEMISTRY, vol. 3, no. 3, June 1977 NEW YORK US, pages 233-238, V. B. KOLOBKOV ET AL. 'A spectral luminescence study of rare-earth activated fluophosphate glasses' * page 233; table 1 *	1,6,7	
X	US-A-4 415 464 (ASAHARA) 15 November 1983 * the whole document *	1	
A	WO-A-87 02656 (ERNST LEITZ WETZLAR GMBH) 7 May 1987 * claims *	2-5	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	25 January 1996	Van Bommel, L

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)